Lesson 15

Kraft Pulp Mills

Lesson Goal and Objectives

Goal

To familiarize you with the pulp production and chemical-recovery processes used in kraft pulp mills, the air emissions generated, and the methods used to reduce pollutant emissions.

Objectives

At the end of this lesson, you should be able to:

1. describe the kraft pulp production process and the chemical-recovery methods used in kraft pulp mills.
2. list at least three pollutants emitted as a result of producing kraft pulp.
3. identify major emission points in the kraft pulp and chemical-recovery process.
4. identify the control equipment or process changes used to reduce emissions at kraft pulp mills.

Introduction

Kraft pulp mills produce the dark-colored wood pulp used in the manufacture of a variety of paper products. Pulp is a viscous slurry of fibrous materials. Liquid is removed from the pulp by passing the pulp over screens and processing it to leave a dried mat of cellulose fibers, or paper. Paper made from kraft pulp is quite strong. The word "kraft" is actually the German word for strong. This paper is used for grocery bags, multiwall sacks, and corrugated cartons. Bleached pulp is used to make printing paper.

Pulp can be made in a number of ways. One of the simplest is to mechanically grind wood in the presence of water to make the slurry. This method, however, produces a weak paper that rapidly deteriorates. Approximately 10% of pulp produced in the United States is made by this method.

Better quality papers can be made from wood pulps produced by chemical methods or a combination of chemical and mechanical methods. Two principal components of wood are cellulose fibers and a material called *lignin*. Lignin is a complex chemical compound which binds the cellulose fibers together. If the hold of the lignin can be weakened, or the lignin eliminated, the cellulose fibers can become free to make strong, durable paper.

A number of processes use mild chemical action to soften wood chips by loosening the hold of the lignin. After softening, the chips are broken apart mechanically to produce the pulp. These processes are termed "semichemical" and "chemimechanical" methods and account for approximately another 10% of the U.S. pulp production.

Full chemical processes actually dissolve the lignin binding the cellulose. The kraft pulping process is a full chemical method which releases the cellulose fibers by dissolving much of the lignin. The good quality papers that result from this method and the efficiency of the chemical recovery methods used in the process have led to its dominance in pulp production. Nearly 80% of the pulps produced in the United States are made by the kraft method.

Kraft Method

The kraft pulping method uses a solution of sodium hydroxide and sodium sulfide to dissolve lignin. This is a fairly straightforward operation. Basically, wood chips are mixed with the chemical solution and cooked in a large pressure cooker (*digester*) until the cellulose fibers are loosened. Because of the high cost and large amount of chemicals used, the kraft method has been designed to recover and regenerate as many materials as possible. The kraft method can be more easily understood if it is separated into two processes as shown in Figure 15-1, pulping and chemical recovery.

The sodium sulfide (Na_2S) which is used in conjunction with sodium hydroxide ($NaOH$) to dissolve the lignin leads to a variety of chemical compounds which are quite odorous. These are produced in the pulping process and can carry through in the various recovery processes. The recovery methods can also emit significant amounts of particulate matter. Therefore, methods for controlling both gaseous and particulate matter emissions are needed in this industry so that air pollution standards can be met.

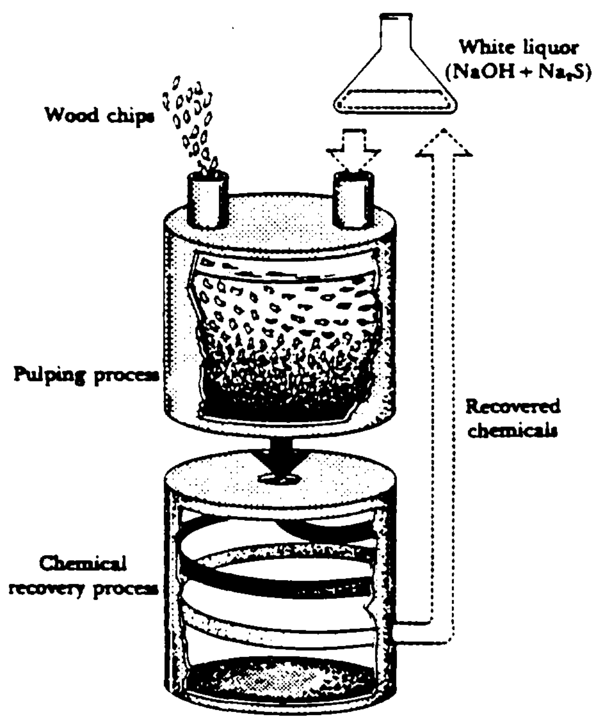

Figure 15-1. Simplified kraft pulping and recovery process.

Pulping Process

A number of different steps are involved in the production of wood pulp. The principal devices used in these steps and shown in Figure 15-2 are

1. the digester,
2. the blow tank, and
3. the brown stock washer.

Initially, pulpwood—which can be obtained from either hardwood or softwood trees—is debarked and chipped. The chips are fed into the digester along with a chemical solution of sodium hydroxide and sodium sulfide in water. This solution is referred to as *white liquor*.

The digesters are tall, cylindrical vessels that cook the mixture of wood and chemicals at temperatures near 180°C (350°F) and at pressures of 760 kPa (110 lbs per square inch). The cooking takes from three to four hours and can be done either continuously or as a batch process.

At the end of the cooking period, the contents of the digester are discharged into a tank. In the blow tank of a batch system, the pressurized mixture is reduced, suddenly, to atmospheric pressure. This change in pressure helps to break up the woody materials and produce the pulp.

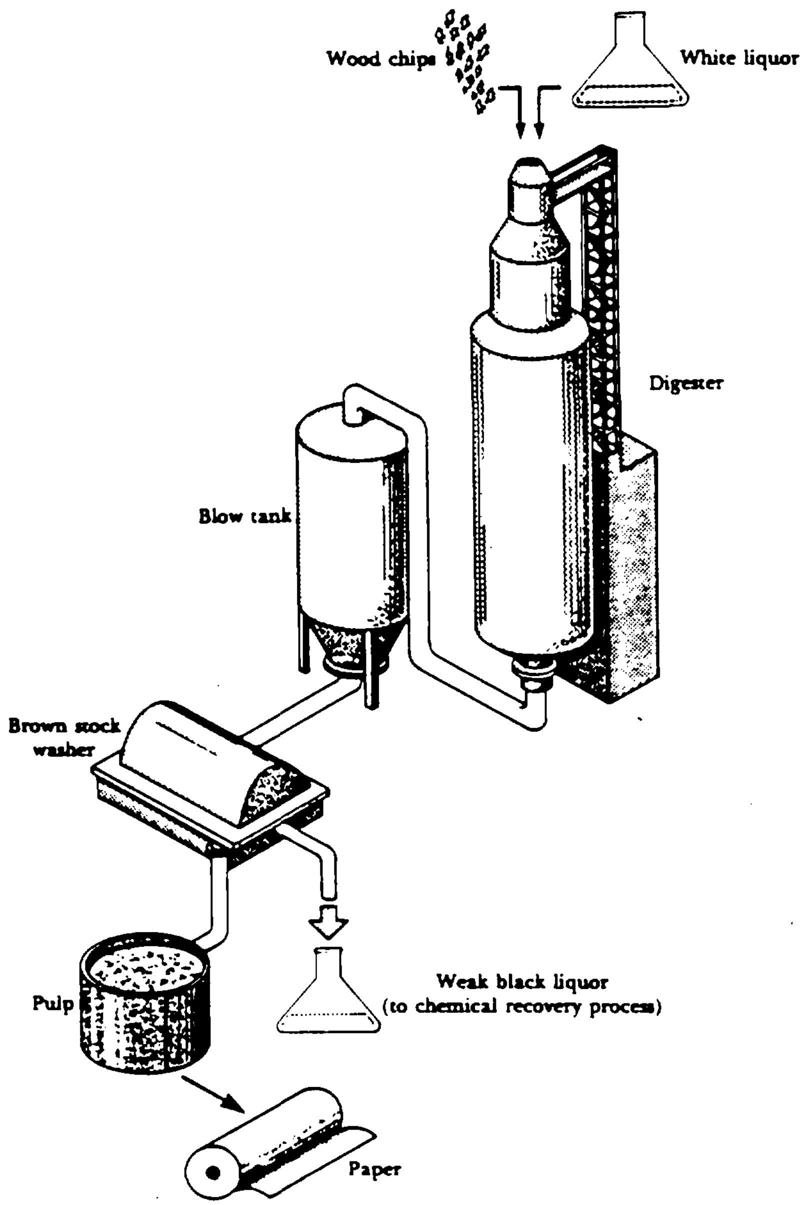

Figure 15-2. Pulping process.

The wood pulp produced is then screened to remove knots and other undissolved materials, diluted, and sent to the brown stock washer (Figure 15-3). Here, the pulp is washed with clean water and separated from the digester chemicals. The cleaned pulp then enters the paper making process where it may be treated and bleached. A continuous mat of cellulose fibers is eventually formed on large screens and then dried and collected as large rolls of paper (Figure 15-4).

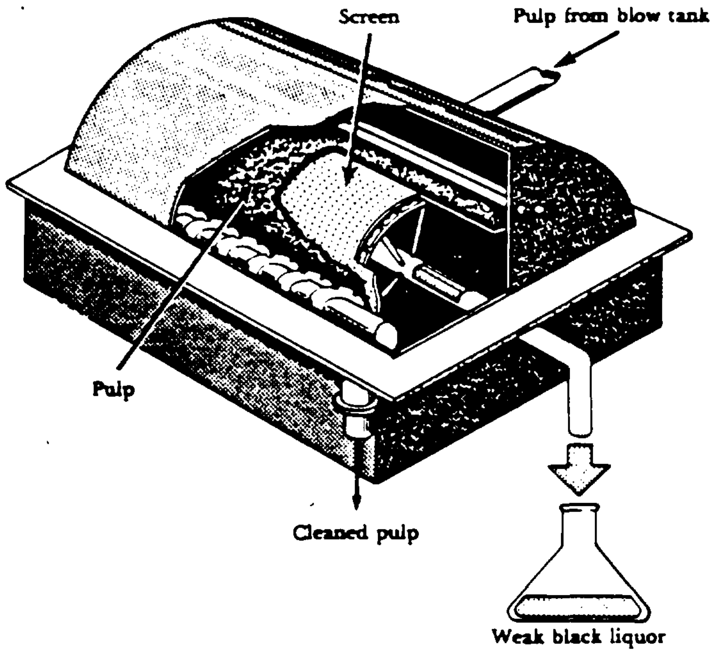

Figure 15-3. Brown stock washer.

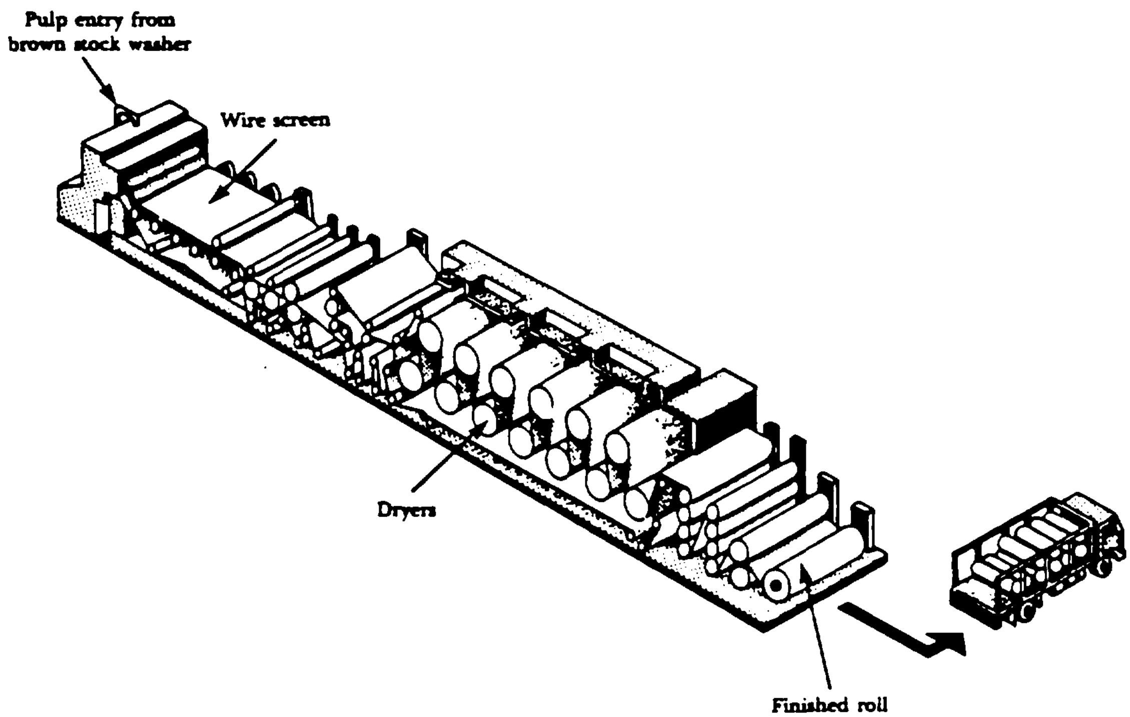

Figure 15-4. Paper making.

The solution of chemicals filtered and washed from the pulp contains complex compounds of dissolved and reacted lignin, organic and inorganic compounds that contain sulfur, and unreacted sodium hydroxide and sodium sulfide. This solution is known as *weak black liquor* because of its color. A principal feature of the kraft pulping process is that most of these materials can be recycled back into the process. Efficient techniques have been developed to recover or regenerate as many chemicals as possible.

Chemical Recovery Process

A larger number of steps are involved in the recovery of chemicals than in the actual pulping process itself. In general, these steps are:

1. evaporation of the weak black liquor,
2. burning of the black liquor concentrate,
3. recovery of sodium sulfide, and
4. recovery of sodium hydroxide.

Kraft pulp mills incorporate each of the four steps listed above. However, the type of equipment used and details of the many recovery and regeneration cycles will vary from plant to plant. Figure 15-5 shows how these steps lead to the recovery of the white liquor solution which is recycled back into the digester with the wood chips. The principal process systems used to perform this recovery are also shown. Each will be discussed in turn with the appropriate recovery step.

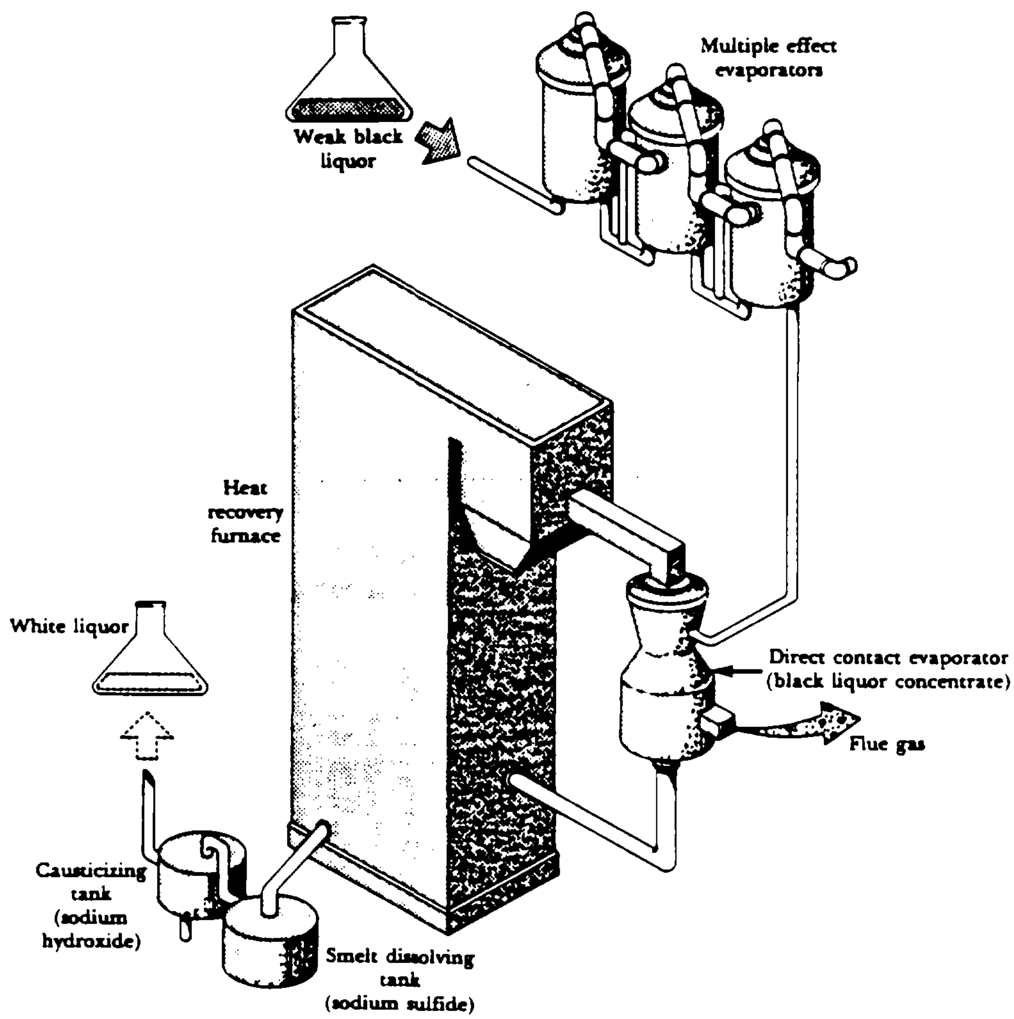

Figure 15-5. Kraft chemical recovery process.

Step 1. Evaporating the Weak Black Liquor

The liquid material collected after filtering and washing the pulp contains reacted or "spent" chemicals. This weak black liquor carries about 15% solid material and a high percentage of dissolved and reacted lignins. Since there is such a high percentage of organic material in the liquor, burning it can provide large amounts of heat for plant operations. Before this can be done, however, much of the water must be removed. This is partially achieved in the multiple effect evaporator system (Figure 15-6), usually consisting of 3 to 8 steam heated condensers. The weak black liquor is reduced in water content as it is passed from one condenser to the other. This produces an increasingly viscous material called *black liquor* having a solids content of 45 to 60%.

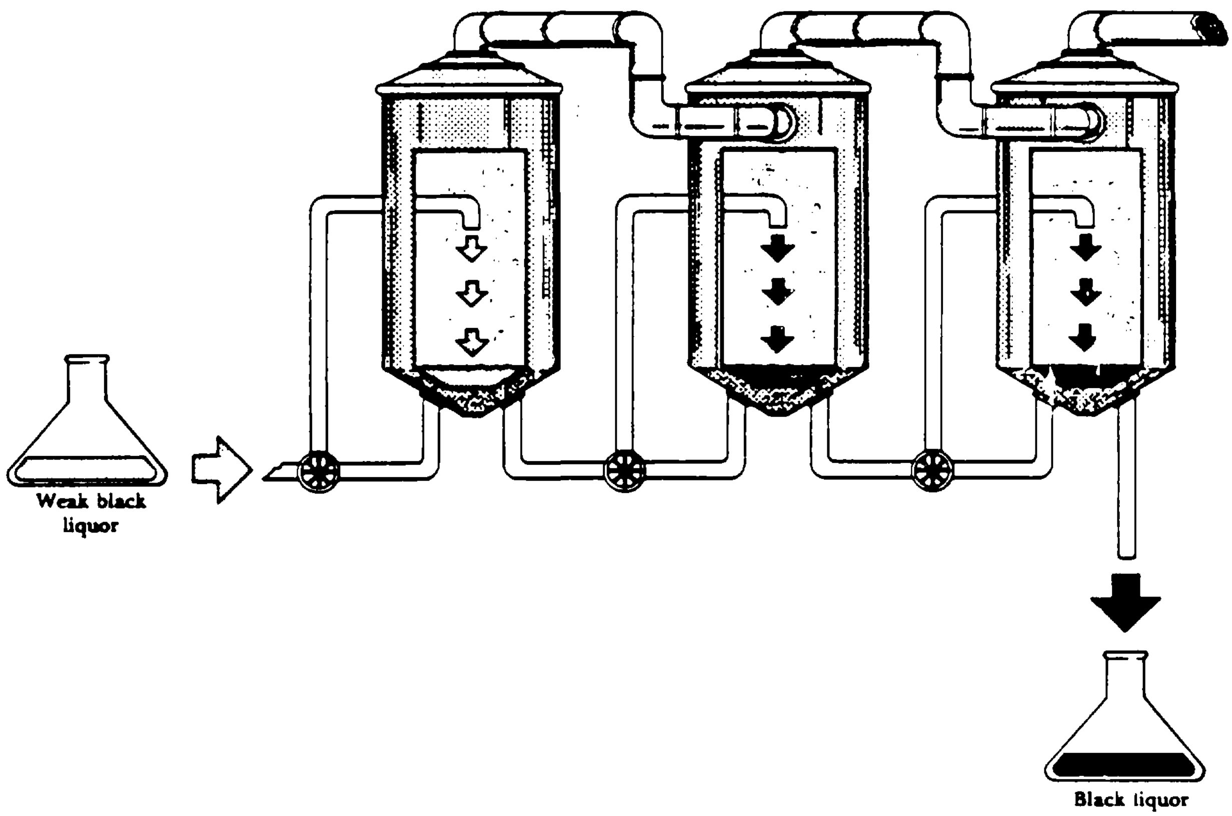

Figure 15-6. Step 1—Multiple effect evaporator system used to produce black liquor.

Because the liquor from the multiple effect evaporator system still has too low a solids content, two concentration methods can be used. In one, a direct contact evaporator is used. Here, hot flue gas emitted from the heat recovery furnace is passed directly through the lower solids liquor to produce the combustible material (Figure 15-7). The idea here is to evaporate the 40% solids black liquor to the point where it will have a solids content near 70%. At this level the concentration of the organic materials will be so high that the liquor will burn. The other method uses one or two additional multiple effect evaporators to concentrate the black liquor solids content, discussed later in this lesson.

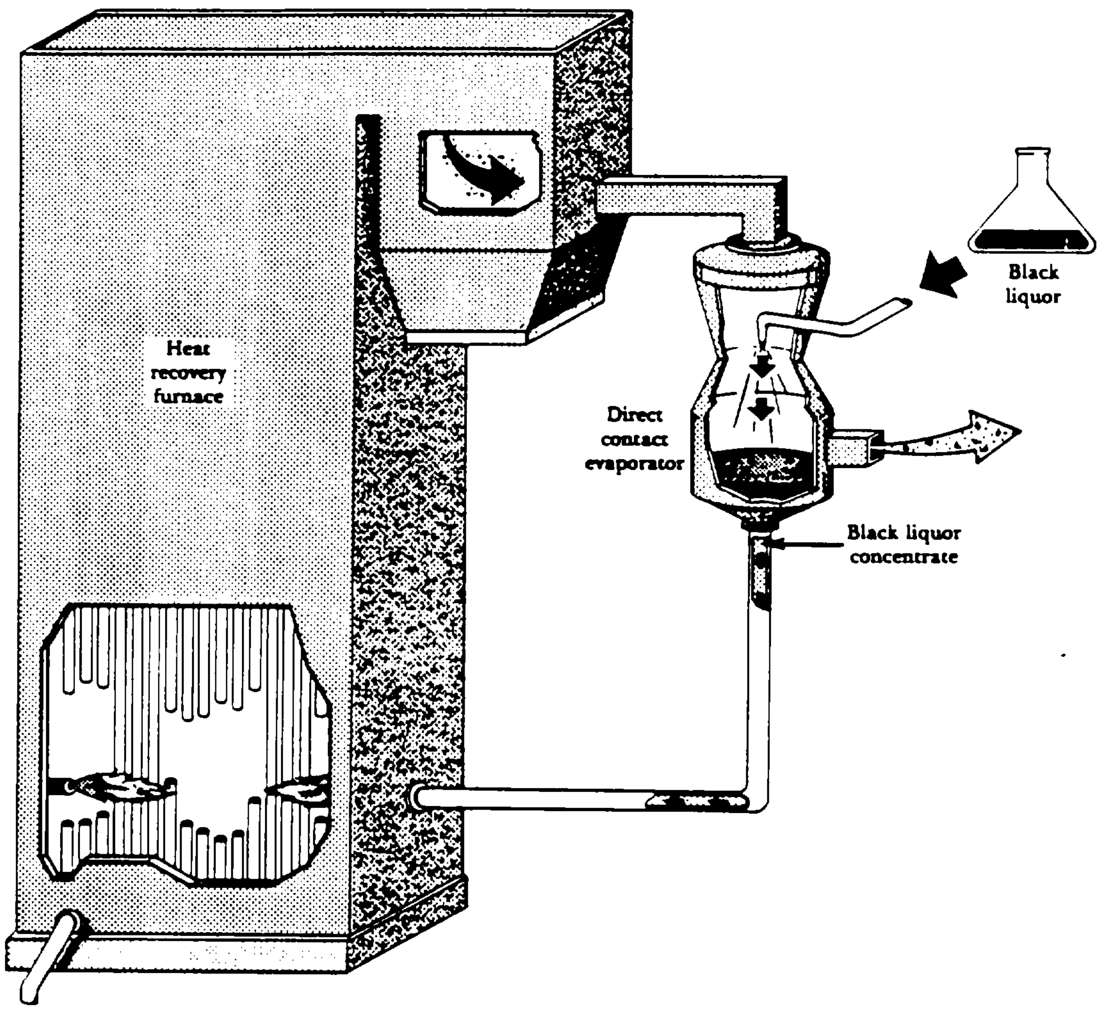

Figure 15-7. Step 1—Direct contact evaporator used to produce black liquor concentrate.

Step 2. Burning the Black Liquor Concentrate

The black liquor concentrate produced in the first recovery step is sprayed into the combustion chamber of the boiler system that is called the black liquor recovery furnace (Figure 15-8). Here, concentrate burns to provide heat and steam for evaporators, digester, driers, and other plant processes.

Since many sodium and sulfur compounds are present in the black liquor along with the combustible lignins, a number of other chemical reactions take place. A molten liquid of inorganic salts, called smelt, is produced as a result of burning the black viscous liquor. The smelt contains both sodium sulfide and sodium carbonate.

The black liquor recovery furnace is the central process system of the whole kraft recovery method. The heat, steam, and chemicals resulting from the combustion of the black liquor cycle back into practically every step of the plant operation.

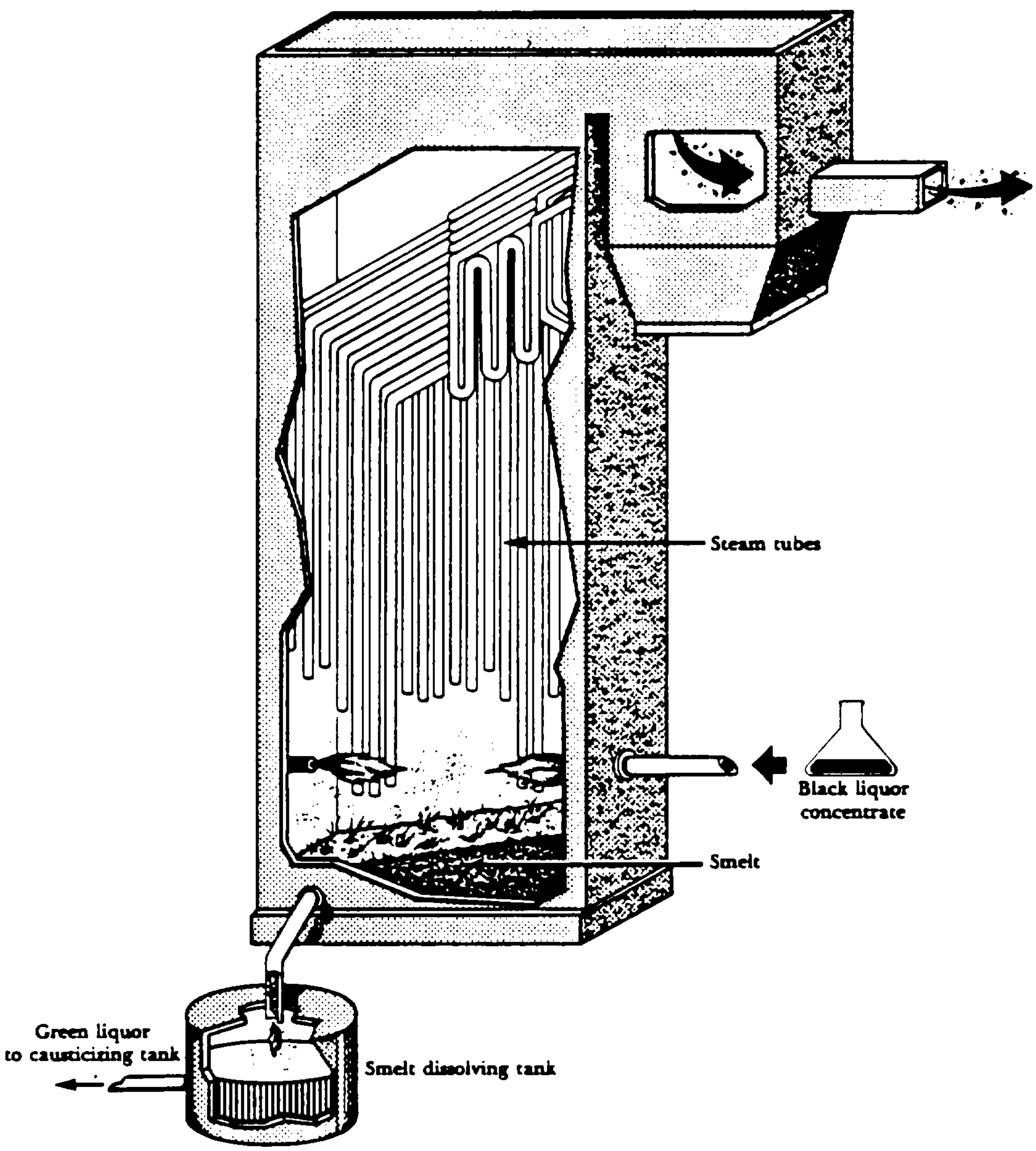

Figure 15-8. Steps 2 and 3—Combustion of black liquor concentrate and recovery of sodium sulfide.

Step 3. Recovering the Sodium Sulfide

The molten salts, or smelt, from the recovery furnace are dissolved in water in the smelt dissolving tank to produce *green liquor*. When the molten salts hit the water in this process, large amounts of steam and particulate matter can be emitted.

The green liquor is principally a solution of sodium sulfide and sodium carbonate (Na_2CO_3). We now have essentially recovered the sodium sulfide (a component of the white liquor) that will be recycled back into the digester. The remaining step is to regenerate sodium hydroxide from the sodium carbonate in the green liquor.

Step 4. Recovering the Sodium Hydroxide

The sodium hydroxide is recovered by treating the green liquor with lime in a causticizing tank. Lime (calcium oxide, CaO) reacts with the sodium carbonate in the green liquor and produces the sodium hydroxide (the other component of white liquor) and also a sludge of calcium carbonate. After this reaction occurs, the resulting solution is clarified and white liquor is obtained.

The white liquor solution of sodium sulfide and sodium hydroxide is then sent back to the digester and the whole process can begin again.

Since the kraft method attempts to recover as many materials as possible, the sludge from the causticizing tank is not discarded today as it was in the past. The calcium carbonate sludge is heated in a lime kiln to regenerate the lime (calcium oxide) used in the causticizing tank. Temperatures vary from 150 to 1300 °C (~ 300 to 2400 °F) along the length of the kiln. Figure 15-9 represents this part of the process. The kiln rotates and can be from 30 to 120 m (100 to 400 ft) in length.

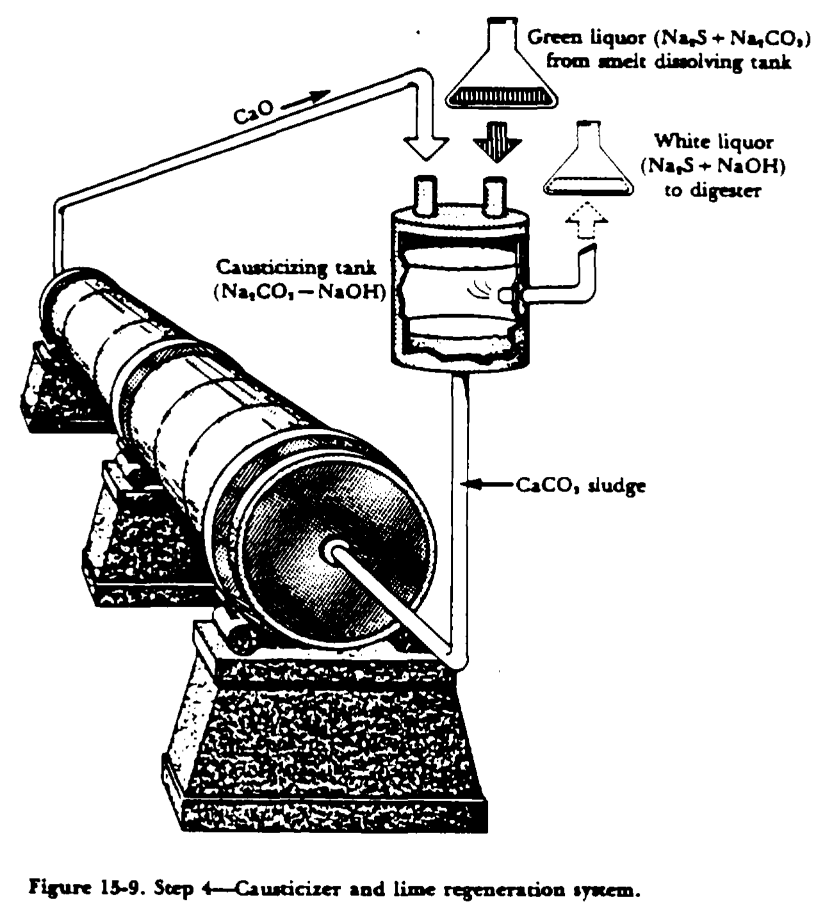

Figure 15-9. Step 4—Causticizer and lime regeneration system.

Other Processes

Other recovery processes are used in kraft pulp mills in addition to those discussed here. For example, turpentine can be condensed from the digester relief gases when pine wood chips are used. Soaps and lignin can be recovered from the weak black liquor for eventual use in a variety of industries.

In order to power the plant operations, boilers that burn gas, oil, coal, bark and wood waste are used. These can supply either steam or electricity to the plant. The black liquor recovery furnace contributes to the power requirements of the plant.

Summary

Figure 15-10 combines the many separate processes that have been discussed here. For review, note that the kraft method can be divided into the pulping process and the chemical recovery process. In the pulping process, wood chips are digested with white liquor—a sodium hydroxide and sodium sulfide solution. In the chemical recovery process, the spent chemicals from the digester are recovered. The black liquor recovery furnace burns the evaporated liquor from the digester to produce both heat and the first component of the white liquor, sodium sulfide. The sodium sulfide is recovered in the smelt dissolving tank, and the second component, sodium hydroxide, is regenerated in the causticizing tank. As a consequence, white liquor is regenerated and sent back to the digester to react with more wood chips.

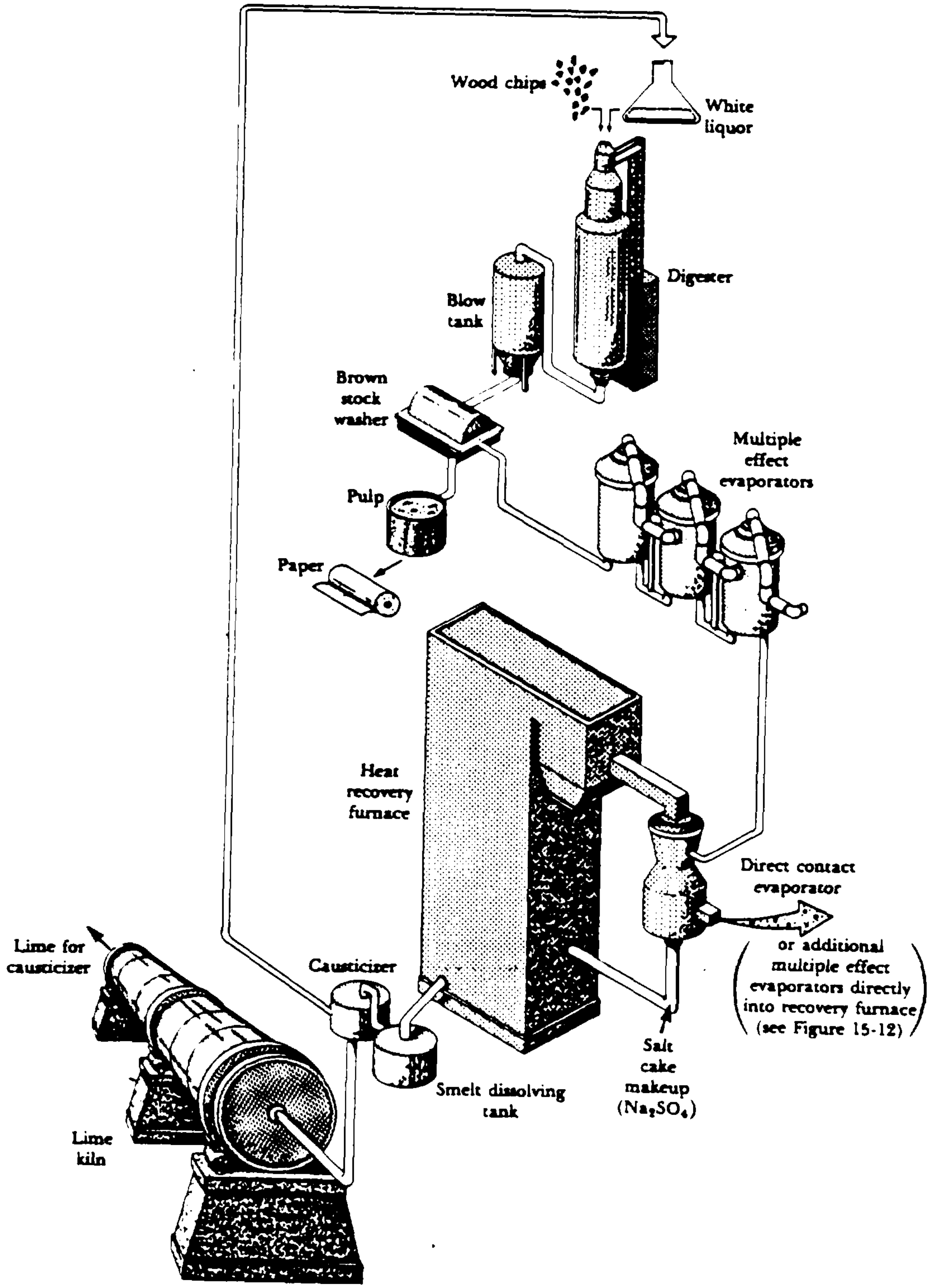

Figure 15-10. Overall kraft process.

Review Exercise

1. Wood pulp is a. a suspension of wood chips in water. b. the material burned in the recovery furnace. c. a suspension of wood fibers in water. d. the final product of the kraft chemical recovery process.	
2. The main purpose of the kraft pulping process is to a. make fine stationery. b. recover chemicals. c. separate lignin from wood fibers. d. make lime.	1. c. a suspension of wood fibers in water.
3. What two compounds are used in the digester to react with and dissolve lignin? a. sodium carbonate and sodium sulfide b. sodium hydroxide and sodium sulfide c. sodium carbonate and lime d. sulfur dioxide and hydrogen sulfide	2. c. separate lignin from wood fibers.
4. Place the following kraft process equipment in proper sequence: blow tank recovery furnace digester smelt dissolving tank multiple effect evaporator causticizing tank brown stock washer direct contact evaporator	3. b. sodium hydroxide and sodium sulfide
5. The purpose of the multiple effect evaporator and direct contact evaporator is to a. produce paper. b. produce black liquor concentrate. c. produce calcium carbonate. d. reduce sulfide emissions.	4. digester blow tank brown stock washer multiple effect evaporator direct contact evaporator recovery furnace smelt dissolving tank causticizing tank
6. Black liquor burned in the recovery furnace produces a. heat and smelt. b. lime and pulp. c. heat and sweat. d. pulp only.	5. b. produce black liquor concentrate.
	6. a. heat and smelt.

7. What is obtained from smelt? a. white liquor b. brown liquor c. black liquor d. green liquor	
8. When in the kraft chemical recovery process is white liquor regenerated? a. while in the lime kiln b. after the green liquor is causticized c. while in the direct contact evaporator d. before it is introduced into the multiple effect evaporator	7. d. green liquor
9. The lime kiln a. produces the lime used in the causticizer. b. produces wood pulp. c. produces sodium sulfide.	8. b. after the green liquor is causticized
10. What are the two principal processes occurring at a kraft pulp mill?	9. a. produces the lime used in the causticizer.
	10. 1. the pulping process 2. the chemical recovery process

Air Pollution Emissions

The introduction of sodium hydroxide and sodium sulfide to dissolve lignin in the kraft pulping process leads to the production of many odorous substances. Among these are hydrogen sulfide, mercaptans (simple organic compounds of carbon, hydrogen, and sulfur), dimethyl sulfide, dimethyl disulfide, and sulfur dioxide. These compounds of sulfur are often measured and described in combination as total reduced sulfur, or TRS. The odor of many of these compounds can be detected even at the part per billion concentration level.

Emissions of sulfur compounds occur in both the pulping and recovery processes. In addition to these gaseous emissions, particulate matter can be released from the black liquor recovery furnace, smelt dissolving tank, lime kiln, and plant power boilers.

The amount and types of pollutants emitted from a kraft pulp mill depend very heavily on how the plant is designed and how it is actually operated. Small changes in temperature, pressure, or chemical composition of separate process steps can have a significant effect on emission levels. In many cases, modifications to the basic process outlined in Figure 15-10 can reduce actual emissions. For example, continuous rather than batch digestion can give better control over the gases emitted. Air or pure oxygen bubbled into the black liquor before it reaches the direct contact evaporator can reduce sulfide emissions. Also, cycling the exhaust from one part of the process into another part can eliminate pollutant gases. For example, organic materials contained in exhaust gases can be incinerated in the lime kiln.

A kraft pulp mill has many possible emission points which are summarized here. Table 15-1 lists the major process systems and types of emissions from each.

Table 15.1. Typical uncontrolled emissions from kraft pulping and recovery processes.

Process	Gas and level		Particulate matter and level	
Digester and blow tank	Hydrogen sulfide Mercaptans	High	–	
Brown stock washer	Hydrogen sulfide Mercaptans	Low	–	
Multiple effect evaporator	Hydrogen sulfide Mercaptans	High	– –	
Recovery furnace and direct contact evaporator system	Hydrogen sulfide Sulfur dioxide	Low	Sodium sulfate Sodium carbonate	High
Smelt dissolving tank	Hydrogen sulfide Mercaptans	Low	Smelt	Low
Lime kiln	Hydrogen sulfide Mercaptans	Low	Sodium salts Calcium carbonate Calcium oxide	High

The emission levels of gases can vary from a few parts per million to tens of thousands of parts per million. References given at the end of this lesson should be consulted for specific data.

Air Pollution Control Methods

Emissions can be reduced at kraft pulp mills by two primary means:

1. modifying plant design and operation, and
2. adding air pollution control equipment.

The most common add-on control devices used in this industry are electrostatic precipitators, wet scrubbers, and incineration systems. In this section, examples of design modifications and applications of add-on equipment will be given.

Modifying Plant Design and Operation

Example 1

Figure 15-8 showed how the hot exhaust resulting from the combustion of organic matter in black liquor can be used to "concentrate" the organic materials before injection into the direct contact evaporator. Direct contact evaporators are merely venturi scrubbers or cascade evaporators. In both systems, the black liquor acts as the scrubbing liquid to remove particles from the recovery furnace exhaust. A 50% removal efficiency can be attained in this manner for particulate matter.

However, a problem arises in using this technique because the carbon dioxide and sulfur dioxide in the flue gas of the recovery furnace can react with chemicals in the black liquor to form hydrogen sulfide. This would result in high sulfur emissions and a loss of sulfur that could otherwise be used in the process. To avoid this, oxygen can be injected into either the weak or the strong black liquor to form compounds that will not convert to hydrogen sulfide. Oxygen can be introduced by using black liquor oxidation systems. These systems are used to treat the black liquor before it goes to the direct contact evaporator (Figure 15-11).

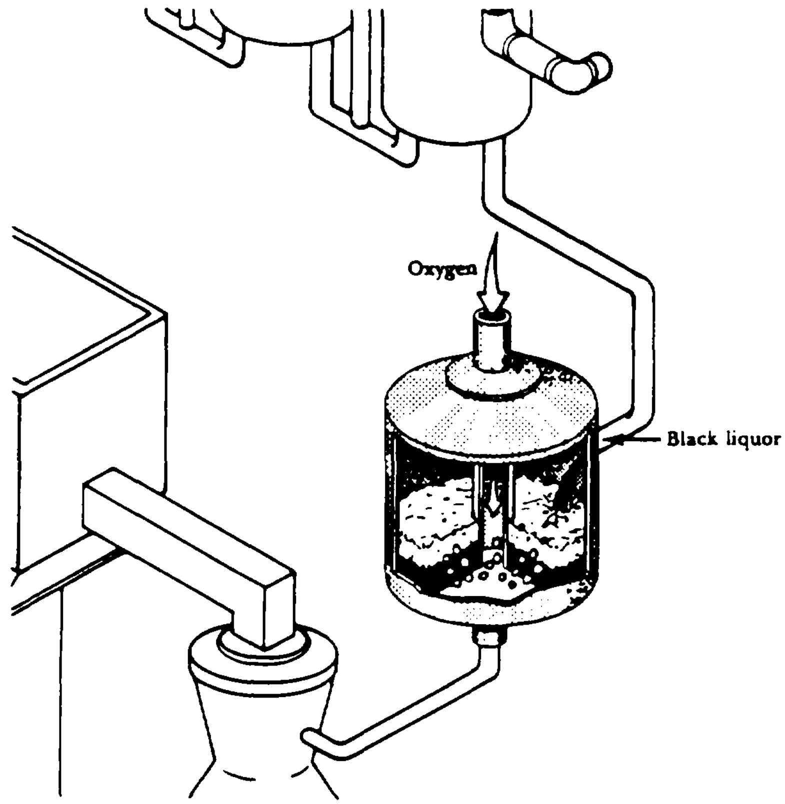

Figure 15-11. Black liquor oxidation system.

Example 2

In many new plants, in order to avoid the problem of hydrogen sulfide formation, black liquor is concentrated without using a direct contact evaporator. One or two multiple effect evaporators are used to concentrate the black liquor, thereby eliminating the need for the direct contact evaporator. In some systems there may be as many as six or seven multiple effect evaporators in series.

These kraft pulp plants do not require the use of oxidation systems. The flue gas from the recovery furnace is usually not scrubbed; the particulate matter is usually removed by using electrostatic precipitators.

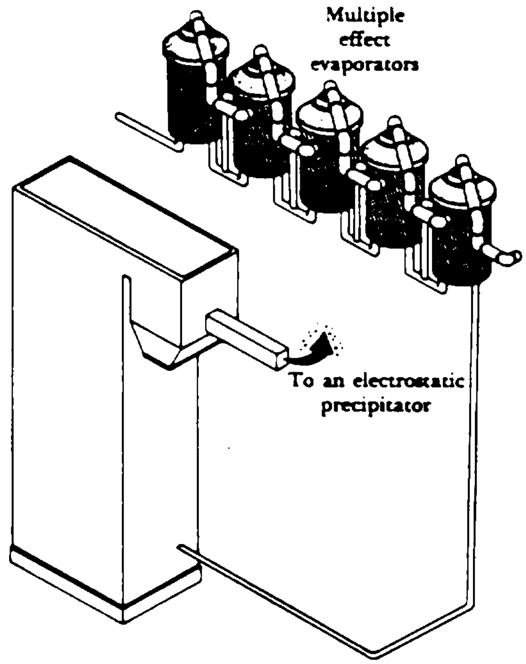

Figure 15-12. Concentrating black liquor using additional multiple effect evaporators.

Example 3

An example of the odorous gas incineration technique is the practice in some plants of collecting the mercaptan and sulfide vapors emitted from the digester, blow tank, and multiple effect evaporators and routing them to the lime kiln, power boilers, or a separate incinerator where they are incinerated.

Another practice is to use the exhaust from the brown stock washers as combustion air for the black liquor recovery furnace.

Adding Air Pollution Control Equipment

Equipment designed specifically for the control of air pollutants is also used at kraft pulp mills. Typical control devices are listed below in Table 15-2.

Table 15-2. Add-on control methods.

System	Control devices
Digester	Incinerators, wet scrubbers
Multiple effect evaporator	Incinerators
Brown stock washer	Incinerators
Recovery furnace	Electrostatic precipitators, wet scrubbers, black liquor oxidation systems
Smelt tanks	Wet scrubbers (venturi, impingement) Demisters (packed tower)
Lime kiln	Wet scrubbers (venturi, impingement), electrostatic precipitators

Electrostatic precipitators are used on kraft recovery systems having direct contact evaporators as well as those using indirect contact evaporators. All of the particulate matter is not removed from the recovery furnace exhaust in the direct contact scrubber, so it is often necessary to install precipitators.

The chemical composition of the liquid used in kraft mill wet scrubbers is often chosen to help in the removal of sulfide gases. Although sized primarily to remove particles emitted from lime kilns or smelt tanks, the absorption that occurs in the scrubbers is important in reducing the emission of sulfur-containing compounds.

New Source Performance Standards

Kraft pulp mills are regulated by States and by the Federal EPA. The Federal standards apply to new or modified kraft pulp mills constructed after September 24, 1976. The emission standards apply to measured total reduced sulfur (TRS) and particulate matter released from specific units of the kraft process. For example, the NSPS regulation limits particulate matter emissions to a level of 0.10 g/dscm (0.044 gr/dscf) from the recovery furnace and 0.1 g/kg of black liquor solids (0.2 lb/ton solids) for emissions from the smelt dissolving tank. Lime kiln particulate emissions are also regulated.

TRS, as measured by the EPA Reference Test Method number 16, is limited to emission levels of from 5 to 25 ppm for the various process units. Table 15-3 summarizes these NSPS emission standards. Depending on plant design, both State and Federal standards might apply to other process units not listed in this table.

Table 15-3. NSPS emission levels.

Process unit	Pollutant	Emission level
Recovery furnace	Particulate*	0.10 g/dscm (0.044 gr/dscf), corrected to 8% oxygen
Smelt tanks	Particulate	0.1 g/kg black liquor solids (dry weight) [0.2 lb/ton black liquor solids (dry weight)]
Lime kilns	Particulate	0.15 g/dscm (0.067 gr/dscf), corrected to 10% oxygen when gaseous fossil fuel is burned 0.30 g/dscm (0.13 gr/dscf), corrected to 10% oxygen when liquid fossil fuel is burned
Digester, brown stock washer, evaporator or black liquor oxidation systems	Total reduced sulfur (TRS)	5 ppm by volume on a dry basis, corrected to a specific oxygen content
Recovery furnaces	TRS	5 ppm by volume on a dry basis corrected to 8% oxygen
Cross recovery furnaces	TRS	25 ppm by volume on a dry basis corrected to 8% oxygen
Smelt tanks	TRS	0.0084 g/kg black liquor solids (dry weight) [0.0168 lb/ton black liquor solids (dry weight)]
Lime kilns	TRS	8 ppm by volume on a dry basis, corrected to 10% oxygen

*Opacity must not exceed 35%.

Review Exercise

1. Pulp mill emissions depend on a. operating variables. b. plant design. c. effectiveness of control equipment. d. all the above	
2. What does TRS stand for? a. Total Recovery System b. Typical Recovery Solvent c. Total Reduced Sulfur d. Tough Research Students	1. all the above
3. Particulate emissions come predominantly from what three processes in a kraft pulp mill?	2. c. Total Reduced Sulfur
4. What are the principal pollutant gases emitted from kraft pulp mills?	3. recovery furnace smelt dissolving tank lime kiln
5. What two types of pollution control techniques are common in the kraft pulping industry? Choose two. a. plant design modification b. hiring private vendors for pollutant removal c. use of bubbles and emission trade-offs d. use of add-on control equipment	4. hydrogen sulfide mercaptans sulfur dioxide dimethyl sulfides dimethyl disulfides
6. Black liquor oxidation systems are used to a. prevent the formation of particulate matter in direct contact evaporators. b. prevent the formation of hydrogen sulfide in the recovery furnace. c. convert black liquor to smelt. d. concentrate black liquor.	5. a. plant design modification d. use of add-on control equipment
7. The direct contact evaporator can do which of the following? a. dewater pulp b. concentrate black liquor c. control particulate matter in the recovery furnace exhaust d. all the above	6. b. prevent the formation of hydrogen sulfide in the recovery furnace.
8. Match up the control device(s) with the process. a. recovery furnace — w. incinerator b. lime kiln — x. baghouse c. multiple effect evaporator — y. electrostatic precipitator z. wet scrubber	7. b. concentrate black liquor c. control particulate matter in the recovery furnace exhaust
	8. a. y, z b. z, y c. w

References

Environmental Protection Agency (EPA). September 1976. *Standards Support and Environmental Impact Statement, Volume 7. Proposed Standards for Performance for Kraft Pulp Mills.* EPA 450/2-76-014a.

Environmental Protection Agency (EPA). April 1979. *Guidance for Lowest Achievable Emission Rates from 18 Major Stationary Sources.* EPA 450/3-79-024.

Environmental Protection Agency (EPA). October 1976. *Environmental Pollution Control Pulp and Paper Industry. Part 1—Air.* EPA 625/7-76-001.

Hendrickson, E. R., Roberson, J. E., Koogler, J. B. 1970. *Control of Atmospheric Emissions in the Wood Pulping Industry—Final Report.* Volumes 1, 2, and 3. Department of Health, Education and Welfare. National Air Pollution Control Administration. EPA-APTD-1234, 1235, and 1236.

U.S. Public Health Service, 1966. *Proceedings from the International Conference on Atmospheric Emissions from Sulfate Pulping.* E. O. Painter Printing Co., DeLand, Florida.